A Study of the Mechanism of Formation of 2,4,6-Perfluoroalkyl-1,3,5-Triazines from Condensation of Perfluoroalkyl Amidines

By

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PRELIMINARY REMARKS

In recording the results of this study a considerable amount of discussion is concerned with preparation and reactions of the N'(perfluoroacylimidoyl)perfluoroalkylamidines. Due to the great number of times it was found necessary to repeat the names of these compounds, it was considered advisable to use the abbreviation "imidoylamidines" where the text permitted. In structural formulas the perfluoroalkyl radical is represented by R_f.

Infrared spectral data were obtained using a Perkin-Elmer Infracord recording spectrophotometer. Ultraviolet spectral data were obtained using a Beckman DK-2 recording spectrophotometer. Chromatographic analyses were obtained using an Aerograph Model A-100-C gas-liquid chromatographic instrument.

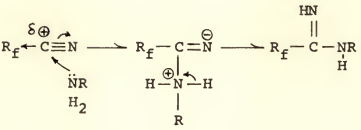
The majority of elemental analyses were determined by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 17, New York. Metal analyses and some Kjeldahl nitrogen analyses were conducted in this laboratory.

All temperatures are reported in degrees centigrade and are uncorrected.

CHAPTER I

INTRODUCTION

In the past several years a considerable amount of work has been done in this laboratory on reactions of the perfluoroalkyl nitriles.[1-5] The presence of the perfluoroalkyl group, unlike the hydrocarbon analog, increases the susceptibility of these compounds to nucleophilic attack. This increased reactivity toward nucleophilic reagents is attributed to the strong electron withdrawing nature of the perfluoroalkyl group. Specifically, the addition of ammonia or amines to the perfluoroalkyl nitriles proceeds with almost the speed of an ionic reaction giving quantitative yields of the corresponding 1,2 addition product.[2]

I 

It has been shown in this laboratory[4] that the perfluoroalkyl nitriles may be trimerized, as a consequence of

their electrophilic character, at relatively low pressures in the presence of basic catalysts to give perfluoroalkyl-substituted sym-triazines. In contrast to this, trimerization of the hydrocarbon nitriles to sym-triazines is generally carried out at high pressures and in the presence of acidic catalysts such as the hydrogen halides.[6,7]

In a somewhat different synthetic approach Reilly and Brown[2] have shown that 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines may be prepared by condensation of the corresponding perfluoroalkyl amidine with the liberation of ammonia.

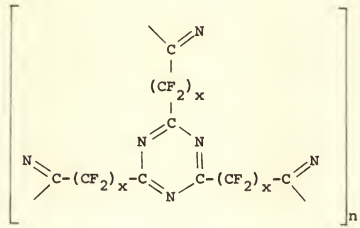
From the standpoint of thermal stability, this particular hetrocyclic system appears rather attractive. Hinkel[8] has shown that sym-triazine is stable to near red heat. The high melting or boiling points of some of the alkyl and aryl substituted sym-triazines suggest that the thermal stability of a number of these compounds is in excess of 300°. It has been found that the perfluoroalkyl-substituted sym-triazines also are stable at temperatures above 300°. One of the suggested uses of the first perfluoroalkyl-substituted sym-triazine, prepared by McBee,[9] was as a heat transfer agent.

In view of the high thermal stability of the sym-triazine ring and the ease with which perfluoroalkyl-

substituted sym-triazines may be prepared, this system appeared particularly suited to the preparation of thermally stable polymers.

Through condensation of the polyfunctional perfluoroalkyl diamidines, Brown[10] has shown that polymeric products may be obtained which are stable when heated at 350° in air. Due to the polyfunctionality of the diamidines the condensation products obtained were highly cross-linked resins and consequently insoluble and infusible materials. The structure proposed for these polymers was a network of triazine rings connected at three points by $-CF_2-$ chains as shown below.

II



In modifying the condensation reaction by co-condensing a monoamidine with a diamidine, Brown[10] found that it was possible to obtain products ranging in physical

properties from that of the highly cross-linked, infusible product described above to intermediate products having elastomeric properties and finally to liquid products, depending on the ratio of the two amidines used. Although the amount of cross-linking was obviously reduced by this method, maximum linearity was in general associated with low molecular weight. The elastomeric products were insoluble and infusible and presumed to be still highly cross-linked.

Since this polymer system showed considerable promise as a useful high temperature elastomer it was considered advisable to make a thorough study of this system and to find a method for preparing a linear polymer chain containing sym-triazine rings connected by perfluoroalkyl groups. As a means of approaching a problem of this nature it seemed advisable to study the condensation reaction of the perfluoroalkyl amidines. In order to circumvent the complexity of studying the condensation of polyfunctional diamidines, monoamidines were used as model compounds.

Statement of the Problem

The major objective of this investigation was to study the condensation of the perfluoroalkylamidines and to determine the mechanism of this reaction, and to further

separate, identify and characterize any intermediate products of the condensation reaction.

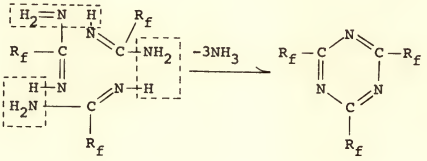
In view of the foregoing introductory remarks a secondary objective, based on the information gained in the mechanism study, was to determine the feasibility of diverting the condensation reaction for the purpose of preparing a sym-triazine substituted with one R_f' and two R_f groups.

CHAPTER II

DISCUSSION

Condensation of Perfluorobutyramidine

In the condensation of the perfluoroalkyl amidines to the perfluoroalkyl-substituted sym-triazines there are required three molecules of the amidine to form the six-membered ring. The probability of this reaction occurring by simultaneous collision of three molecules, with loss of ammonia, was considered unlikely.

III 

Since a termolecular reaction is in general quite rare, it was felt that the condensation of the amidines to form the sym-triazine ring would proceed through a two- or three-step process and the various steps in the reaction

sequence might be noted in a study of the kinetics of the reaction. Although it was realized that the reaction was in all probability quite complex kinetically, it was felt that some indication of intermediate products of the reaction might be noted which would give some idea of the mechanism involved.

In the first deammonation experiment a solution of perfluorobutyramidine in pentachloroethane was heated to 110° and the rate of evolution of ammonia was determined. Periodically during this experiment small samples were removed from the reaction mixture to follow changes in the infrared spectra of the reactants. In following this change it seemed probable that any new species being formed would result in the disappearance or appearance of an absorption maxima. In addition, it would be possible to determine when triazine was first formed since the intense absorption maxima at 6.4μ, corresponding to C=N stretching frequency, is characteristic of the conjugated perfluoroalkyl-substituted sym-triazines.[2]

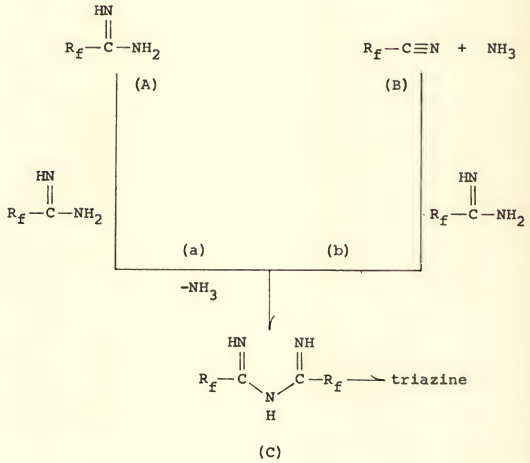
It was observed in the early experiments in the deammonation of perfluorobutyramidine that the first appearance of infrared absorption at 6.4μ occurred at a period in the reaction when approximately one-third of the total

theoretical amount of ammonia had been evolved. With the assumption that for each mole of ammonia evolved, one-third of a mole of triazine was being formed, the calculated amount of triazine at this period in the reaction was far in excess of that indicated by the infrared spectra. In addition to this, at termination of the reaction the calculated amount of triazine which should have been present, based on the total amount of ammonia evolved, far exceeded the room temperature solubility of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine in pentachloroethane. Upon cooling the reaction mixture to room temperature only a single liquid phase was found, revealing that far less triazine was present than indicated by the amount of ammonia evolved.

On the basis of these observations it appeared that the amidine was condensing to give a stable intermediate compound which in turn was reacting to give the final product, 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. A reasonable explanation of the initial reaction occurring appeared to be a "dimerization" reaction rather than a simple decomposition of the amidine into the volatile nitrile and ammonia, since no nitrile was observed as a product of the reaction. Of the two possible modes of reaction suggested by these results IV(a) appears more likely on the basis of

the volatility of the perfluorobutyronitrile involved (b.p. 0°).

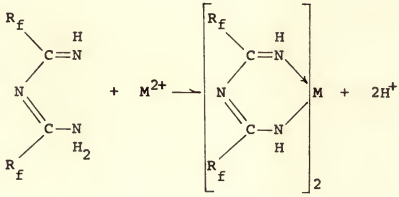
IV



Lending support to this postulated mechanism was the report by Schaeffer[11] proposing a mechanism for the deammonation of trichloroacetamidine suggesting an intermediate similar to that shown above as IV(C) and also the preparation of a compound both by Schaeffer[11] and by Dachlauer[12]

similar to IV(C), where in place of R_f was the trichloromethyl radical. Their preparation of this compound was carried out by reaction of trichloroacetonitrile with aqueous ammonia.

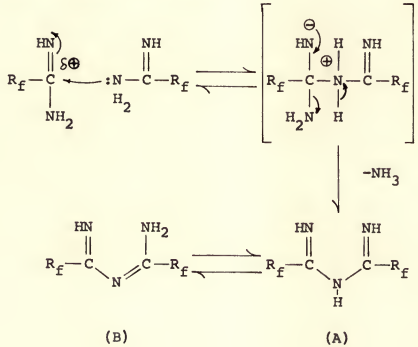
A number of attempts were made to isolate this proposed compound, IV(C), from reaction mixtures containing a considerable amount of solvent but these attempts were not successful. At this stage in the research the possibility was realized that the proposed intermediate should form chelates with suitable metal ions since chelation would result in the formation of a favored six-membered ring.

V 

By eliminating the use of a solvent system, in the deammonation of perfluorobutyramidine, the proposed intermediate was isolated from the deammonation mixture as its copper(II) chelate and subsequently identified as N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate.

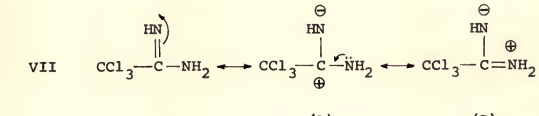
With the evidence presented thus far a tentative mechanism may be proposed for the initial step in the condensation of the perfluoroalkylamidines. It is proposed that the strongly electron-withdrawing nature of the perfluoroalkyl group decreases the electron density about the carbon atom of the amidine group presenting an electron-deficient site for attack by the unshared electrons of an amino nitrogen of a second amidine molecule. Subsequent loss of ammonia would give VI(A).

VI



In contrast to the above mechanism, Schaeffer[11] proposed a mechanism for the deammonation of trichloro-

acetamidine suggesting attack by the imino nitrogen in its polar canonical form VII(A).



VII

(A) (B)

In the present study, attack by the imino nitrogen would appear to be less probable due to destabilization of this form by the strong electron-withdrawing perfluoroalkyl group. At this stage in the research no concrete evidence was available to substantiate either mechanism since, regardless of the actual mode of attack, the resultant product would probably be a tautomeric mixture as VI(A) and VI(B).

Evidence obtained in subsequent experiments,* which permitted structural assignments to be made, very strongly suggests attack by the amino group.

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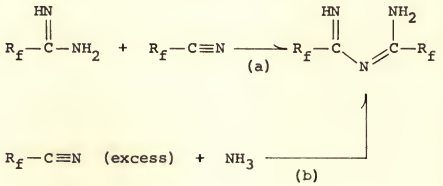
*Under "Structure of N'(Perfluoroacylimidoyl)perfluoroalkylamidines and Some Related Compounds" see discussion concerning the structure of N(perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine, p. 23.

Preparation of the N'(Perfluoroacylimidoyl)perfluoroalkylamidines

In following the above reasoning and with the basicity of the amidines in mind, it was obvious to assume that the amidines should readily react with the perfluoroalkyl nitriles to yield a product identical with that obtained in the condensation of the amidines. It was, in fact, found that the perfluoroalkyl amidines reacted rapidly and quantitatively with the perfluoroalkyl nitriles to give N'(perfluoroacylimidoyl)perfluoroalkylamidines, VIII(a). A modification of this reaction procedure, which eliminated the need for preparing the amidine, required only reaction of anhydrous ammonia with an excess of the nitrile, in sealed ampule, to yield an identical product, VIII(b).



VIII

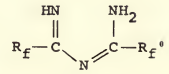
It may be noted in the above reactions that reaction VIII(a) presents a method for the preparation of compounds having two different R_f groups, compounds very difficultly available through condensation of a mixture of amidines.

At this point in the research a series of imidoyl-amidines were prepared having different R_f groups; the properties of these compounds are shown in Table 1. The first member of the series, where R_f is CF_3, is a white, low-melting solid which decomposes slowly at room temperature to a liquid-solid mixture of undetermined composition. This compound apparently has thermal stability similar to that of the corresponding perchloro compound described by Schaeffer.[11] Compounds in the series in which R_f is C_2F_5 or C_3F_7 or combinations of unlike R_f groups are water-white liquids having a sharp ammoniacal odor. The lower molecular weight compounds were found to be sufficiently stable to be distilled at reduced pressure.

The imidoyl-amidines hydrolized slowly when in contact with atmospheric moisture; the initial product of hydrolysis was the relatively stable acylated perfluoro-alkyl amidine.

TABLE 1

N°(PERFLUOROACYLIMIDOYL) PERFLUOROALKYLAMIDINES

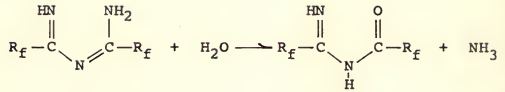


R_f	R_f°	b.p. °C	d^{25}	n^{25}	Nitrogen calcd.	Nitrogen found
CF_3	CF_3	38-42 (m.p.) [a]	--	--	20.28	19.16
C_2F_5	C_2F_5	35.9-36.1 (6.8 mm.)	1.613	1.3438	13.67	13.41
C_3F_7	C_3F_7 [b]	44.3-44.7 (1.5 mm.)	1.685	1.3386	10.31	10.50
CF_3	C_3F_7	50.0-50.8 (13.0 mm.)	1.652	1.3508	13.67	13.51
C_2F_5	C_3F_7	39.2-40.0 (3.8 mm.)	1.656	1.3398	11.76	11.38
C_3F_7	C_7F_{15} [c]	--	--	--	--	--

[a] Decomposes at room temperature.

[b] Analysis: Calculated: C, 23.58; F, 65.35. Found: C, 23.74; F, 65.11.

[c] Isolated only as its copper(II) chelate.

IX 

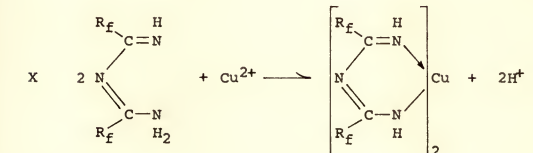
The structure of this hydrolysis product was confirmed by comparison of the hydrolysis product of N'(perfluorobutyrimidoyl)perfluorobutyramidine with that of the compound prepared by acylation of perfluorobutyramidine with perfluorobutyric anhydride. The melting points and infrared spectra of these compounds were identical. Further confirmation was obtained by elemental analysis.

The weakly basic nature of the amino group of the imidoyl-amidines is shown by the instability of their acid salts toward water. When the hydrochlorides of the imidoyl-amidines are dissolved in water a heavy liquid precipitate results which is found to be the free imidoyl-amidine showing that these compounds are less basic than water.

Metal Chelates of the N'(Perfluoroacyl-imidoyl)perfluoroalkylamidines

The metal chelates of the N'(perfluoroacylimidoyl) perfluoroalkylamidines were prepared in essentially quantitative yields by reaction with the corresponding metal

acetates. A typical example of chelate formation is that of reaction of N'(perfluorobutyrimidoyl)perfluorobutyramidine with cupric ion, where R_f is C_3F_7.



It was possible to follow the course of this chelation reaction by determining the change in pH on addition of a standardized copper acetate solution. As shown in Figure 1 a total pH change of about 1.5 units was observed over the entire reaction with a sharp break occurring in the titration curve. The end point of the reaction was calculated to be equivalent to a quantitative reaction of the ligand with cupric ion. Following the equivalence point the presence of excess copper acetate forms a buffered system with the resultant decrease in hydrogen ion concentration. It was possible to confirm the molecular weight of some of the ligands by this method.

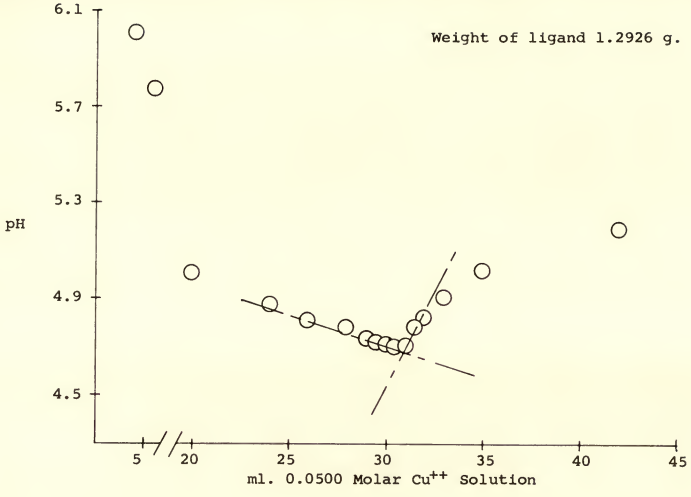


FIGURE 1

TITRATION OF N'(PERFLUOROBUTYRIMIDOYL)PERFLUOROBUTYRAMIDINE

The physical properties of the metal chelates are shown in Table 2. The metal chelates were found to be soluble in a wide variety of polar organic solvents, less soluble in non-polar solvents and insoluble in water.

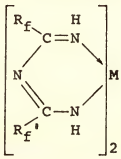
Since copper(II) forms square planar complexes a search was made for possible geometric isomers in those chelates formed from imidoyl-amidines with unlike R_f groups. No evidence was found that indicated the presence of such isomers.

The absorption spectra of the metal chelates in the visible region of the spectrum were determined as a method of characterization and the observed maxima are shown in Table 2 along with descriptive colors as exhibited by the chelate in the crystallizing solvent. The copper and nickel chelates, with their unfilled subshells, formed colored chelates and those of zinc and mercury, with their completed subshells, formed the expected colorless compounds.

Characterization of the metal chelates and the ligands in the ultraviolet region of the spectrum proved to be of considerable interest in providing evidence for subsequent structural assignment of the N'(perfluoroacyl-imidoyl)perfluoroalkylamidines and additional compounds containing the imino group.

TABLE 2

N'(PERFLUOROACYLIMIDOYL) PERFLUOROALKYLAMIDINE METAL CHELATES



Ligand		Metal	Color[a]	Absorption Maxima[b]		
R_f	R_f'			Max. m	Log	Max. m
CF_3	CF_3	Cu	maroon[e]	500 394	1.69 1.87	282
C_2F_5	C_2F_5	Cu	maroon[f]	485 400	1.65 1.85	285
C_3F_7	C_3F_7	Cu	maroon[f]	490 405	1.69 1.89	285
C_3F_7	C_3F_7	Zn	white[f]	--	--	290
C_3F_7	C_3F_7	Ni	orange[f]	492	1.72	241 305
C_3F_7	C_3F_7	Hg	white[f]	--	--	289
CF_3	C_3F_7	Cu	maroon[f]	500 396	1.65 1.84	284
C_2F_5	C_3F_7	Cu	maroon[g]	490 405	1.67 1.87	284
C_7F_{15}	C_3F_7	Cu	maroon[f]	490 405	1.73 1.92	286

[a] As solution in crystallizing solvent.
[b] Spectroscopic data determined on methanol solutions of the metal chelate using a Beckman DK-2 recording spectrophotometer.

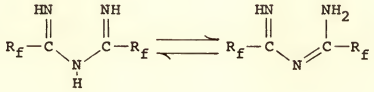
TABLE 2.--Extension

Log	m.p. °C	Analysis			
		Metal[c] %		Nitrogen[d] %	
		Calcd.	Found	Calcd.	Found
4.13	223 dec.	13.35	13.19	17.67	17.52
4.00	134-135	9.40	9.34	12.43	12.02
4.35	148.5-149.5	7.26	7.21	9.58	9.67
4.18	108.5-108.8	7.41	7.31	9.58	9.39
4.37 3.75	152-153	6.77	6.66	9.64	9.52
3.83	126-127	19.93	20.39	8.30	8.53
4.15	114-115	9.40	8.97	12.43	12.10
4.06	102-103	8.18	8.08	10.82	10.56
4.18	135-136	4.98	4.86	6.58	6.46

[c] Copper, nickel and zinc determined electrolytically. Mercury determined as HgS.
[d] Analysis by Kjeldahl method.
[e] Crystallized from benzene.
[f] Crystallized from carbon tetrachloride.
[g] Crystallized from hexane.

Structure of the N'(Perfluoroacylimidoyl)perfluoroalkylamidines and Some Related Compounds

In making the initial proposal of the structure of the first condensation product of the perfluoroalkyl amidines it was recognized that these compounds probably existed in tautomeric equilibria as shown below. No evidence was

XI 

(A) (B)

available at the time to determine which of the two species was present in the higher concentration, the "keto" or the "enol" form.

In characterization of the imidoyl-amidine metal chelates and a representative ligand, N'(perfluorobutyrimidoyl)perfluorobutyramidine, it was found that the ligand exhibited an absorption maximum at 262 mμ ($\log \epsilon_{max.}$ 3.93); whereas a comparative spectrum of a compound containing an isolated imino group, as in perfluorobutyramidine, exhibited no maxima above 220 mμ (Table 3). Since in

TABLE 3

ULTRAVIOLET ABSORPTION MAXIMA OF SOME FLUOROCARBON DERIVATIVES CONTAINING THE IMINO GROUP*

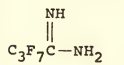
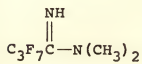
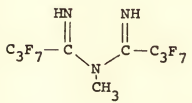
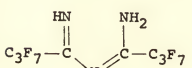
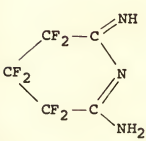
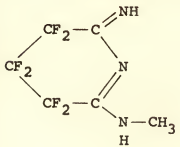
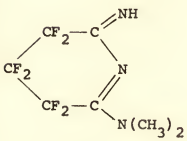
Compound	$\lambda_{max.}$, mμ	log $\epsilon_{max.}$
	<220	--
	232	3.84
	230**	--
	262	3.93
	254	4.22

TABLE 3.--Continued

Compound	$\lambda_{max.}$, mμ	log $\epsilon_{max.}$
	259	4.23
	276	4.28

*Spectroscopic data were determined on methanol solutions of the compounds with a Beckman DK-2 recording spectrophotometer.

**Inflection point. No maximum above 220 mμ.

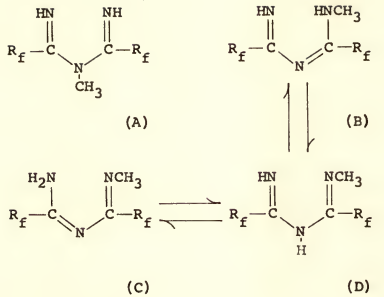
structure XI(A) the imino groups may be considered as two isolated chromophores this structure would not be expected to exhibit absorption above 220 mμ. It would appear reasonable then to assign the conjugated structure XI(B) as the predominant structure of the imidoyl-amidines.

In an attempt to further substantiate the assignment of a conjugated structure to the imidoyl-amidines several other fluorocarbon derivatives containing the imino group were prepared. These compounds are shown in Table 3.

In the preparation of the first compound in this series it was reasoned that N(perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine could be present as either of two isomeric structures, XII(A or B), with the further possibility of two additional tautomeric structures, XII(C and D).

The tautomeric structures XII(B, C and D), being similar to the structure proposed for the unsubstituted imidoyl-amidines, would be expected to exhibit absorption in approximately the same region of the spectrum, with some shift toward longer wave lengths due to the auxochromic effect of the methyl group. On the other hand substitution of a methyl group on the central nitrogen, as in structure XII(A), would remove any possibility of tautomerism. In

XII



(A) (B) (C) (D)

this unconjugated structure, absorption would be expected in an area of the spectrum approximating that of N-methyl perfluorobutyramidine. As shown in Table 3, no maximum is observed above 220 mμ for this compound, thus establishing the structure of N(perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine as XII(A), in which the methyl group is located on the central nitrogen atom. The absence of any maximum above 220 mμ for this compound further substantiates the conjugated structural assignment previously proposed for the unsubstituted imidoyl-amidines, XI(B).

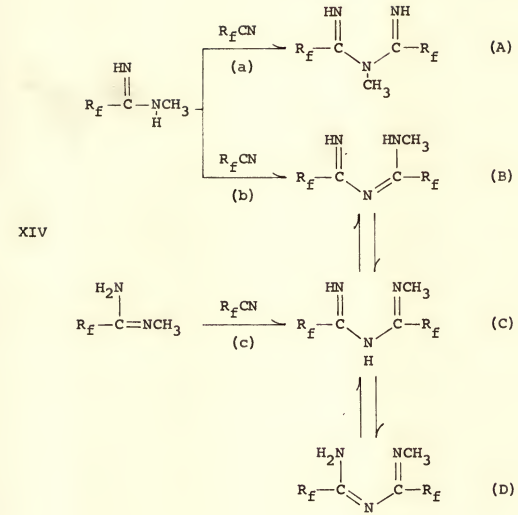
Some divergence at this time would seem appropriate in order to discuss the probable mechanism of this reaction and its relation to the condensation of the perfluoroalkyl-

amidines, since a definite structural assignment may be made for these compounds.

In the preparation of N-methyl-substituted imidoyl-amidine by the reaction of an excess of nitrile with methyl amine, we may visualize an initial 1,2 addition of methyl amine to the nitrile, XIII.

XIII $R_f-C\equiv N + CH_3NH_2 \longrightarrow R_f-\underset{\underset{\text{(A)}}{\text{HN}}}{\overset{\|}{C}}-\underset{\text{H}}{\text{N}}CH_3 \rightleftharpoons R_f-\underset{\underset{\text{(B)}}{\text{NH}_2}}{\overset{|}{C}}=NCH_3$

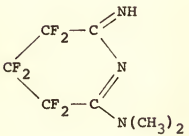
The initial amidine formed may react with excess nitrile present to give the final N-methyl imidoyl-amidine, XIV. As indicated, the N-methyl amidine may conceivably exist in two tautomeric forms, XIII(A and B), and attack on the nitrile may occur by the unshared electrons of either the imino or the amino nitrogen. Although three reasonable modes of attack are presented, XIV(a, b and c), two modes give rise to the tautomeric structures XIV(B, C and D); whereas the third mode of attack, by the N-methyl amino group, as in XIV(a), would give a single unconjugated structure XIV(A), as previously assigned this compound.



This would then indicate that the methyl amino nitrogen is the attacking nucleophile and by analogous reasoning this observation would lend support to the previously proposed mechanism for the condensation of the amidines where the amino nitrogen is the attacking group.

Preparation of N,N-dimethyl perfluoroglutarimidine[10] provided a compound having only one possible conjugated structure (XV).

XV

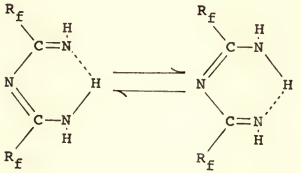


This compound was found to absorb at 276 mμ (log $\epsilon_{max.}$ 4.28). By successive removal of the substituent methyl groups a shift in absorption maxima to shorter wave lengths was observed, similar to that found on comparing the spectra of N,N-dimethyl-perfluorobutyramidine and perfluorobutyramidine, Table 3. It would appear from this that although the unsubstituted and N-methyl perfluoroglutarimidines may exist in unconjugated tautomeric forms, their predominant structure is that of the conjugated form and the shift in wave length of absorption on methylation is due entirely to the auxochromic effect of the methyl group.

It is possible from the above discussion to draw further conclusions regarding the structure of the imidoyl-

amidines. Due to the similarity of the imidoyl-amidines to the perfluoroglutarimidines, it would seem reasonable to expect that the wave length at which absorption occurs for these compounds would be very close to that of perfluoroglutarimidine. Finding that there is a shift in the absorption maxima for the imidoyl-amidines to a longer wave length than that shown for perfluoroglutarimidine supports the view that there is a further contribution to the resonant structure through intra-molecular hydrogen bonding (XVI).

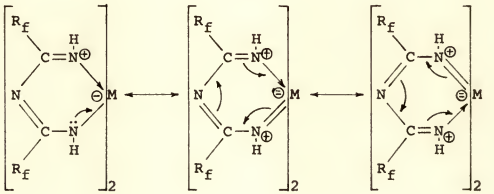
XVI



The net effect would be a reduction in electronic restraint causing the observed shift in the absorption maxima.

A bathochromic shift was also observed on substitution of metal ions for the "chelated" proton in that the ultraviolet absorption maximum occurred at a shorter wave

length than for the free ligand.* Figure 2 shows comparative spectra of N'(perfluorobutyrimidoyl)perfluorobutyramidine and its copper chelate. This shift toward the red is in general associated with covalent donor-metal bonding. The observed shift would indicate considerable metal-donor interaction and further imply an extension of the conjugated system through multiple metal-nitrogen bonding presenting a benzenoid-type structure.

XVII 

This type of resonance has been suggested by Calvin[15] based on chelate stability constants. In addition Pauling[16] and Brockway and Cross[17] have demonstrated that

*The nickel chelate differed in that two major maxima were observed, one at a lower frequency and one at a higher frequency than the free ligand.

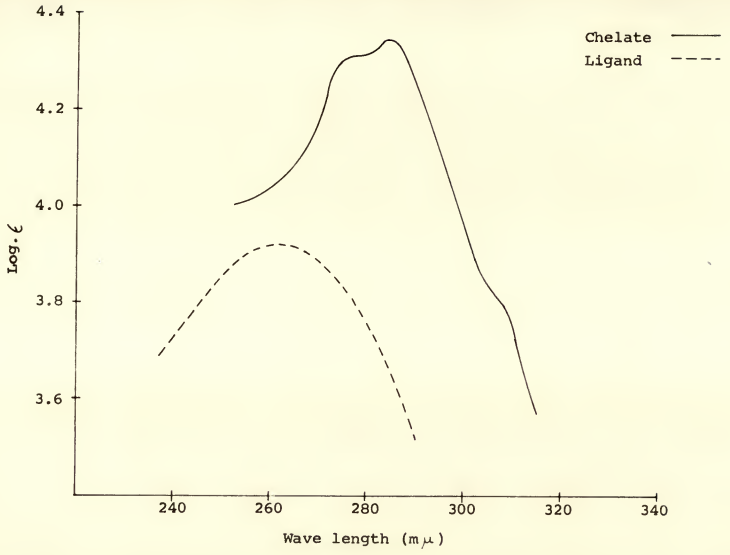
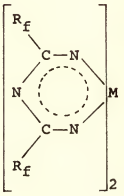


FIGURE 2

ULTRAVIOLET SPECTRA OF N'(PERFLUOROBUTYRIMIDOYL) PERFLUOROBUTYRAMIDINE AND ITS COPPER(II) CHELATE IN METHANOL

double bonds of this type are indicated for ordinary covalent complexes of the metals. Substantiating evidence would seem to lie in the fact that the free ligand is hydrolytically unstable whereas in the form of a metal chelate there is exhibited a considerable increase in hydrolytic stability. This increase in hydrolytic stability on formation of the chelate would suggest a decrease in localization of charge, XXIII, thus presenting little or no charged site for attack.

XVIII



Infrared Assignments for the N'(Perfluoroacylimidoyl)perfluoroalkylamidines and Some Related Compounds

Assignments of the principal absorption maxima of N'(perfluorobutyrimidoyl)perfluorobutyramidine and its copper chelate are shown in Table 4 with those of other fluorocarbon derivatives having similar structural features.

TABLE 4

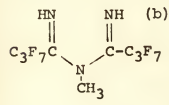
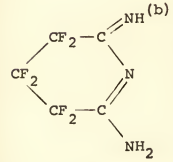
INFRARED ABSORPTION SPECTRA ASSIGNMENTS
IN THE 2.5-6.6 μ REGION*

Compound	N-H			N-D	
	Asym. Str.	Sym. Str.	Assoc.	Asym. Str.	Sym. Str.
$C_3F_7C(=O)-NH_2$ (a)	2.82 (m)	3.03 (m)	--	4.00 (m)	4.30 (m)
$C_3F_7C(=NH)-NH_2$ (b)	2.86 (m)	3.05 (m)	--	3.85	to
$C_3F_7C(=NH)-N=C(NH_2)-C_3F_7$	2.86 (m)	3.00 (w)	3.20 (w,br)	3.87 (m)	4.07 (m)
$[C_3F_7C(H)=N-C(C_3F_7)=N-Cu]_2$ (b)	--	2.93 (w)	--	--	4.00 (w)

TABLE 4.--Extension

	-C=N str.		-C=N str. (deut.)		N-H
Assoc.	C=NH	-C=N-	-C=ND	-C=N-	Def.
--	C=O 5.85 (s)		C=O 6.02 (s)		6.15 (m)
4.01[c]	5.71 (m, d) 5.97 (s) 6.10 (m, d)	--	5.75 (w, d) 6.06 (s) 6.20 (w, d)	--	--
4.24 (w)	6.13 (s)	6.30 (s)	6.17 (s)	6.36 (s)	6.60 (w)
--	6.25 (s)	6.45 (s)	6.29 (s)	6.47 (s)	6.54 (m, d)

TABLE 4.--Continued

Compound	N-H			N-D	
	Asym. Str.	Sym. Str.	Assoc.	Asym. Str.	Sym. Str.
 (b)	--	2.86 (m) 3.10 (m)	--	--	3.90 (m) 4.19 (m)
 (b)	--	3.00 (m, d)	3.22 (m)	--	4.09 (m)

(a) Nujol mull
(b) Kel-F Polymer Oil mull
(c) triplet
(d) shoulder
(e) liquid state
(m) medium
(s) strong
(w) weak
(br) broad

TABLE 4.--Extension

	-C=N str.		-C=N str. (deut.)		N-H
Assoc.	C=NH	-C=N-	-C=ND	-C=N-	Def.
--	5.95 (s) 6.06 (s)	--	5.95 (s) 6.03 (s)	--	6.17 (m, d)
4.39 (m)	6.10 (m)	6.30 (s)	6.10 (m, d)	6.30 (s)	5.90 (m)

*Infrared spectra determined using a Perkin-Elmer Infracord. Instrument reproducibility $\pm$ 0.03 μ.

Assignments were made between 2.5 and 6.6 μ and, in general, the absorption maxima observed in this region can be well correlated with the proposed structures; however, some anomalous maxima were observed.

Little difficulty was encountered in making assignments for N-H stretching frequencies for all the compounds with the exception of N(perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine. Some difficulty arises in this assignment in that two maxima appear, having approximately the same intensity, at 2.86 and 3.10 μ . In view of the rather convincing evidence for structural assignment previously described where the compound was assigned a structure having two unconjugated imino groups it would appear that separate N-H stretching maxima occur for each imino group. In the deuterated compound a normal shift* is

---

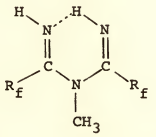
*The approximate magnitude of this effect may be readily calculated for an X-Y bond if the bond force is assumed to be directly proportional to the displacement from the equilibrium position. In accordance with Hooke's Law then we may write

$$\nu = \left(\frac{1}{2\pi c}\right)\left(\sqrt{\frac{K}{\mu}}\right)$$

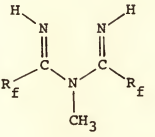
where ν is the frequency of the stretching vibration in reciprocal centimeters, C is the velocity of light, K is the force constant of the bond and μ is the reduced mass of the

observed at 3.90 and 4.19 μ respectively substantiating that both these maxima were due to N-H stretching. Without additional evidence it is tentatively suggested that this doublet may be attributed to the predominance of structure XIX(A) which would presumably be stabilized through intramolecular hydrogen bonding.

XIX



(A)



(B)

Structure XIX(B) would be expected to exhibit only a single maximum for N-H stretch; however, an additional possibility may be considered in that symmetric and asymmetric stretch, in XIX(B), may be infrared active and give rise to the

---

system. The ratio of X-D to X-H absorption frequency may be readily calculated as

$$\frac{\nu_{X-D}}{\nu_{X-H}} = \sqrt{\frac{2 + M}{2 + 2M}}$$

where M is the atomic weight of atom X. For the present study where X is nitrogen this ratio is equal to 0.73.

observed doublet. Further supporting evidence of the diimino type structure for this compound is found in the region of 6 μ where a doublet is observed at 5.95 and 6.06 μ for the C=N stretching frequency. This type of splitting is frequently observed for β di-carbonyl compounds; the similarity of this compound to that of the β di-carbonyl compounds would support the assigned diimino structure. A shoulder appearing at 6.17 μ was assigned to N-H deformation. This shoulder was not present in the deuterated compound.

In attempting to make assignments for C=N stretching frequency and for that of N-H deformation frequency it was found that these two maxima occur in approximately the same region of the spectrum, around 6 μ. In order to differentiate between absorption maxima due to these structural features, each of the compounds shown in Table 4 was synthesized with hydrogen replaced by deuterium. The shift in the absorption frequency on replacement of hydrogen by deuterium permitted the assignment of N-H deformation maxima for the compounds shown in Table IV. Unfortunately these assignments could only be made on the basis of a disappearance of an absorption maximum since N-D deformation occurs in the strong C-F stretching region of the spectrum.

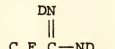
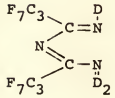
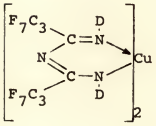
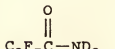
Definite assignments were made for N-H deformation in N'(perfluorobutyrimidoyl)perfluorobutyramidine at 6.60μ and for its copper chelate at 6.54μ. No deformation assignment was made for perfluorobutyramidine. Apparently in this compound the N-H deformation is completely obscured by the C=N stretching maximum.

It is interesting to note that the maxima at 6.13 and 6.30μ in the spectra of N'(perfluorobutyrimidoyl)perfluorobutyramidine, which can now be definitely assigned to C=N stretching, are shifted to slightly longer wave lengths on formation of the copper chelate. This shift would be consistent with increased conjugation as proposed previously for the metal chelates.

It was noted in this infrared study that the deuterated compounds contained some hydrogen. In obtaining infrared spectra of N'(perfluorobutyrimidoyl)perfluorobutyramidine-d_3 it was found that deuterium was exchanging rapidly with hydrogen on exposure of the compound to atmospheric moisture. Since varying rates of exchange were also noted for the other deutero compounds, the approximate rate of exchange was determined; the results are shown in Table 5.

TABLE 5

APPROXIMATE RATE OF DEUTERIUM EXCHANGE

Compound	Rate
	Detectable exchange in 24 hours
	Detectable exchange in 15 minutes
	Considerable exchange in 2 minutes
	No exchange in 24 hours
	Complete exchange in 1 minute*

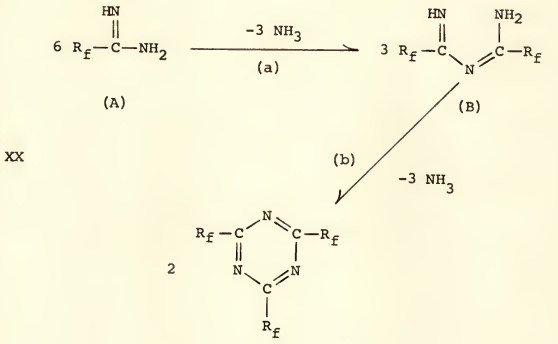
*Perfluorobutyramide-d_3 warmed in H_2O at 60° for 1 minute.

It is of interest to note the difference in the rate of exchange for N'(perfluorobutyrimidoyl)perfluorobutyramidine-d_3 and its copper chelate. The free ligand shows extensive exchange in a matter of minutes whereas on chelation with copper the deuterium is relatively insensitive to exchange, showing no change in 24 hours.

Pyrolysis of N'(Perfluorobutyrimidoyl)perfluorobutyramidine

Following the characterization of the N'(perfluoroacylimidoyl)perfluoroalkylamidines, the next phase in the research, in following the original objective, was to determine the mechanism of the subsequent steps in the condensation of the amidines. Although it was determined quite clearly that initially "dimerization" of the amidine occurs yielding the imidoyl-amidine, at this point in the research no experimental evidence was available to clarify the next step in the reaction, XX(b).

Since methods, at this time, were available for the preparation of the imidoyl-amidines the first necessary experiment was the pyrolysis of these compounds to prove that condensation would occur as shown in XX(b). Examination of the stoichiometry in the reaction sequence below shows,



obviously, that this step is a considerably more complex reaction than the initial one, XX(a). The complexity of the reaction seemed to preclude any possibility of a study of the kinetics of the reaction; however, a quantitative determination of the pyrolysis products was considered necessary since it was apparent that cleavage of the imidoyl-amidine must occur which could give rise to a number of by-products.

In the initial experiment N'(perfluorobutyrimidoyl)-perfluorobutyramidine was heated above 100° in a system swept with dry nitrogen and all condensable gaseous products

were collected in a liquid, air-cooled trap. On periodic examination of the products collected and determination of the molecular weight of the gases, it was found that a number of products were being trapped and the molecular weight of the evolved gases was not constant throughout the run. The products collected included solids, liquids and gases which were subsequently identified as perfluorobutyramidine, N'(perfluorobutyrimidoyl)perfluorobutyramidine, perfluorobutyronitrile and ammonia. The low volatility of the imidoyl-amidine and the amidine excluded the possibility of their having been transferred from the reaction flask to the liquid air trap since they would have had to pass a water-cooled condenser and an ice-cooled trap. The only possible conclusion was that gaseous decomposition products from the imidoyl-amidine were transferring in the gaseous state through the ice-cooled trap and condensing in the liquid air trap. When the frozen gases were melted, either amidine, imidoyl-amidine or both formed, depending on the relative concentration of ammonia and nitrile present.

The high-boiling liquid which remained in the reaction flask was identified as 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. It was thus clear that step XX(b) may occur.

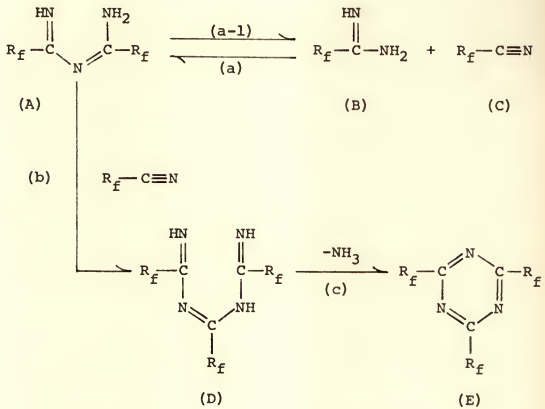
As further proof that perfluorobutyronitrile is a pyrolysis product of N'(perfluorobutyrimidoyl)perfluorobutyramidine, a second experiment was carried out where the evolved gases were passed first through a tube packed with phosphorus pentoxide which removed all the ammonia. The trapped gas in this experiment was identified by its molecular weight (Dumas) and infrared spectra as perfluorobutyronitrile.

An additional question arose concerning the possibility of the coexistence of ammonia and perfluorobutyronitrile as a gaseous mixture without reaction occurring. These gases were mixed, with reaction taking place only at an extremely slow rate. This observation served to explain the change in molecular weight observed in the first pyrolysis experiment.

Reaction of Perfluoropropionitrile with N'(Perfluorobutyrimidoyl)perfluorobutyramidine

In the previously described pyrolysis of N'(perfluorobutyrimidoyl)perfluorobutyramidine it was shown that a product of this reaction was perfluorobutyronitrile. The appearance of the nitrile as a product of this reaction was presumed to be due to cleavage of the imidoyl-amidine

as shown in the following reaction sequence XXI(a). Since this nitrile has a boiling point of 0° some would presumably escape from the reaction mixture.



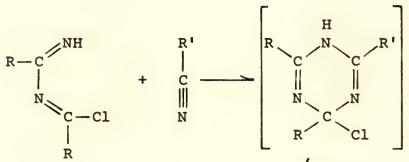
This mechanism proposes an addition of an imidoylamidine to a nitrile, resulting in an intermediate XXI(D) which, on the loss of ammonia, yields the perfluoroalkyl-substituted sym-triazine. In order to show that this reaction scheme is an actual representation of the mechanism, three approaches were considered as possible proof. (1) A

kinetic study of the decomposition of an N'(perfluoroacyl-imidoyl)perfluoroalkylamidine. (2) Isolation of the intermediate XX(D). (3) Indirect interpretation by examining the products of reaction of a nitrile with an imidoyl-amidine in which the nitrile contains an R_f group different from those of the imidoyl-amidine.

The kinetic approach was considered of such a complex nature, due to probable multiple equilibria involved, that the data obtained would be of little interpretive use. The second method, isolation of the intermediate XXI(D), was tried on a limited basis by heating the imidoyl-amidine in the presence of excess nitrile, but the only products isolated were the original imidoyl-amidine and the perfluoroalkyl-substituted sym-triazine. The third method appeared to be the most promising approach since analysis of the final product, triazine, would be an implication of the probable mechanism.

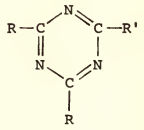
A similar type of study was conducted by Grundmann and co-workers[13] in an attempt to elucidate the mechanism of nitrile trimerization to sym-triazines. They noted that polymerization was usually catalyzed by hydrogen halides and found it possible to isolate an intermediate reaction product of easily trimerizable nitriles. An empirical

formula for this adduct, as given by Troger,[14] was $(RCN)_2 \cdot HCl$. A "diene" condensation was proposed as a reaction scheme. Some of their experimental results, however, indicated this to be an oversimplification; when the HCl-trichloroacetonitrile adduct, XXII(A) where R is CCl_3, was treated with acetonitrile, no 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine was obtained; whereas, when a mixture of trichloroacetonitrile and acetonitrile was treated with hydrogen chloride a 90 per cent yield of this product was obtained.



(A) (B)

XXII



(C)

In considering the possibility of a different mechanism wherein the imidoyl-amidine adds to the nitrile followed by a cyclo-elimination reaction, it was considered probable that reaction of the NH_2 group of the imidoyl-amidine with a nitrile should be similar to the reaction of an amidine with a nitrile. It appeared, however, that due to greater delocalization of electron density, the reactivity of the NH_2 group of the imidoyl-amidine would be less than that of the amidine NH_2. This decrease in nucleophilicity of the imidoyl-amidine is exemplified by experimental evidence where reaction of the amidines with excess nitrile at controlled low temperature resulted in a quantitative conversion to the imidoyl-amidine with no intermediate XXI(D) or triazine present. When the reaction temperature was increased, however, triazine was formed as a by-product or as the major product of the reaction, dependent on reaction conditions used.

This experiment showed that the increase in temperature was sufficient to cause reaction of the imidoyl-amidine with nitrile to occur, steps XXI(b and c). On the basis of evidence available at this point in the research the qualitative order of energies of activation of the various reaction steps was assumed to be XXI($a > b > a_{-1} > c$). The

validity of this assumption could be demonstrated by reacting an imidoyl-amidine with a nitrile containing a different R_f group than the imidoyl-amidine if the reaction were carried out at a temperature below which equilibria XXI(a, a_{-1}) occur. Under these conditions one of the major products would be a sym-triazine having one R_f' and two R_f groups.

Under the conditions employed in studying this reaction in which an equimolar mixture of N'(perfluorobutyrimidoyl)perfluorobutyramidine was allowed to react with perfluoropropionitrile in a sealed ampule the resultant product predicted would be predominantly a mixture of two triazines, $(C_3F_7CN)_2(C_2F_5CN)$ and $(C_2F_5CN)_3$, based on reaction sequence XXI(b and c). The latter product, $(C_2F_5CN)_3$, would arise from reaction of the C_2F_5CN with ammonia evolved in the cyclization step, XXI(c).

Vapor phase chromatographic separation of the reaction products in the first experiment, run at 130°, revealed that the product was composed of a mixture of all four possible perfluoroalkyl-substituted sym-triazines, the greatest proportion being the predicted compound (Table 6). It appeared from the results of this experiment that the two additional triazines present were due to decomposition of

TABLE 6

PERFLUOROPROPIONITRILE--N' (PERFLUOROBUTYRIMIDOYL) PERFLUOROBUTYRAMIDINE REACTION PRODUCT DISTRIBUTION

Reaction Temperature	Molar Ratio[a] of Reactants	Time at Temperature Hrs.	Conversion to Triazine %
130	1:1[b]	2.0	--
110	1:1	1.5	5
80-85	1:1	67.5	52
65	1:1	75.0	35
65	1:1	123.0	53
100-105	(c)	35.0	--
65	(d)	78.0	--
20-30	(e)	7,200.0	73
--	(f)	--	--
--	(g)	--	--

(a) Molar ratio of $R_f-C(=HN)-N=C(NH_2)-R_f$ to $R_f'-CN$ where R_f' is C_2F_5 and R_f is C_3F_7.

(b) Reaction product refluxed for 24 hours prior to chromatographic analysis.

(c) Reaction of 2:1 molar ratio of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine with 2,4,6-tris(perfluoroethyl)-1,3,5-triazine in the presence of NH_3.

TABLE 6.--Extension

Triazine Product Distribution %			
$(R_f'CN)_3$	$(R_f'CN)_2(R_fCN)$	$(R_fCN)_2(R_f'CN)$	$(R_fCN)_3$
2	21	45	32
3	24	41	32
3	21	46	30
3	20	44	33
3	20	45	32
3	21	46	30
4	23	44	29
14	37	37	12
3.7	22.2	44.4	29.6
12.5	37.5	37.5	12.5

(d) R_f' is CF_3.

(e) Room temperature decomposition of N'(perfluoropropionylimidoyl)perfluorobutyramidine.

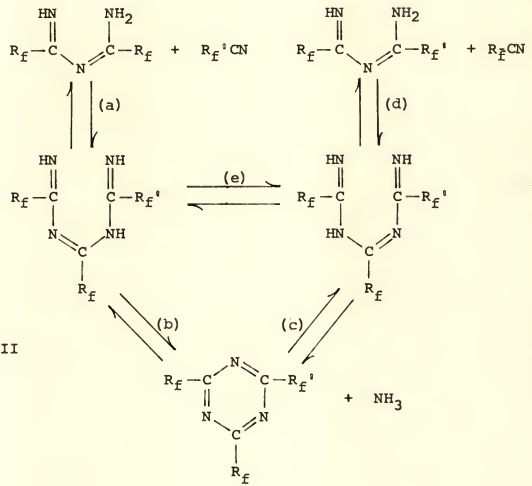
(f) Calculated random distribution of R_f to R_f' groups on the triazine ring where R_f to R_f' ratio is 2:1.

(g) Calculated distribution as in (f) where R_f to R_f' ratio is 1:1.

the imidoyl-amidine, as in equilibrium XXI(a, a_{-1}), giving rise to perfluorobutyronitrile. Subsequent reactions were carried out at progressively lower temperatures in an attempt to prevent this decomposition. It was found, however, that regardless of the temperature at which the reaction was conducted or the reaction time, for a given molar ratio of reactants, the same product distribution was obtained (Table 6).

This series of experiments indicated that there still remained the possibility that equilibrium XXI(a, a_{-1}) was operative even at low temperatures (65°). In order to determine if this equilibrium was the cause of the presence of the two additional triazines in the product mixture, an experiment was carried out in which N'(perfluorobutyrimidoyl)perfluorobutyramidine was heated in vacuo for 181 hours at 65°. Chromatographic examination of the product, at the end of this time, revealed that approximately 50 per cent of the imidoyl-amidine had been converted to 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. It was apparent from this experiment that the imidoyl-amidine was decomposing at 65° and presumably equilibrium XXI(a, a_{-1}) was occurring even at this low temperature. Although decomposition of the imidoyl-amidine in the presence of a foreign nitrile

could be responsible for the observed triazine product mixture, other complicating factors were considered. Equilibria at XXI(b and c) and a possible tautomeric equilibrium, as shown in XXIII(e), could also contribute to the observed mixture.



XXIII

A relatively simple experiment proved that an equilibrium does exist at XXI(c) and by implication also at XXI(b). A 2:1 molar mixture of triazines, $(C_3F_7CN)_3$ and

$(C_2F_5CN)_3$, was heated in an ampule in the presence of anhydrous ammonia, and the resultant products identified chromatographically. The product of this reaction was found to be essentially identical to the mixture of triazines that was previously found when reacting a nitrile with an imidoyl-amidine (Table 6). This same reaction does not occur in the absence of a basic catalyst.

In a private communication, Dr. R. D. Spencer* pointed out that the percentages of each of the four triazines observed in this study agree closely with those shown in Groenweghe's report** for the random reorganization of two different groups among three sites. As shown in Table 6 the experimental distribution and the calculated distribution are quite similar. The possibility of determining mathematically the product distribution of such a complex reaction appears to be unusual and presumably may be attributed to the similarity in reactivity of the nitriles involved.

In contrast to the similarity of reactivities of the perfluoroalkylnitriles, proposed above, Dachlauer[20] and

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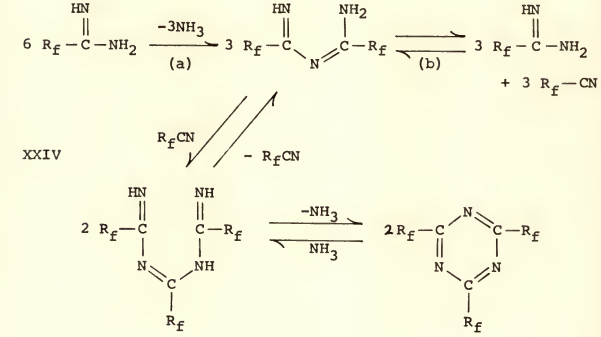
**Research Department, Inorganic Chemical Division, Monsanto Chemical Company.

later Grundmann[13] treated a mixture of trichloroacetonitrile and acetonitrile with hydrogen chloride and obtained good yields (90 per cent) of 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine.

This last series of reactions showed quite clearly that the overall mechanism of the thermal condensation of the perfluoroalkylamidines is extremely complex involving a number of simultaneous equilibria. It is felt, however, that on the basis of the experimental evidence presented a reasonable mechanism may be proposed (XXIV).



The question may arise in viewing the above mechanism whether the reaction of ammonia with triazine would show

some evidence of the presence of imidoyl-amidine. In limited attempts at a reaction of this nature no imidoyl-amidine nor amidine was found. Considerable difficulty is encountered in attempting this reaction due to an interfering reaction. Ammonia reacts with triazine at low temperatures (room temperature) to give a solid triazine-ammonia complex of unidentified composition and structure. At elevated temperatures this adduct decomposes yielding triazine and ammonia.

Attempted Reaction of N'(Perfluorobutyrimidoyl)perfluorobutyramidine Hydrochloride with Perfluoropropionitrile

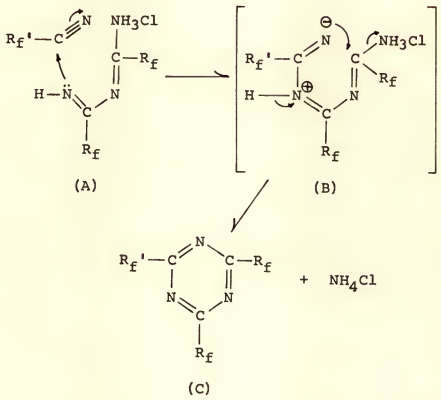
In the previous discussion the experimental evidence revealed the over-all complexity of the mechanism of the condensation of the perfluoroalkylamidines. It was obvious that the addition of a foreign nitrile to an imidoyl-amidine would invariably give a mixture of four perfluoroalkyl-substituted triazines in the presence of the basic condensation product, ammonia. In order to pursue the secondary objective of this research it was necessary to provide a reaction which would yield a quantitative method for the preparation of a sym-triazine containing two different perfluoroalkyl substituents. A reaction of this nature would

present a method for the preparation of a perfluoroalkyl-substituted sym-triazine ring incorporated in a linear polymer chain.

In an extension of the reaction discussed in the previous section, reaction of an imidoyl-amidine hydrochloride with a nitrile was considered. The by-product of this reaction would be ammonium chloride, thus eliminating the possibility of equilibria XXIII(b and c) from occurring, and in addition, the imidoyl-amidine would presumably be stabilized in the form of a salt. Although it appeared probable that the nucleophilicity of the NH_2 group of the imidoyl-amidines would be destroyed in forming the hydrochloride, it seemed probable that under suitable high temperature reaction conditions the imino nitrogen would act as the nucleophile. The attack by the imino nitrogen on the nitrile, with elimination of ammonium chloride, would form the desired sym-triazine, XXV(C).

When this reaction was carried out by reacting N'(perfluorobutyrimidoyl)perfluorobutyramidine hydrochloride with perfluoropropionitrile in the presence of an excess of hydrogen chloride, only a small amount of liquid product was obtained. However, chromatographic analysis revealed this liquid to consist of 89 per cent of 2,4,6-tris(perfluoro-

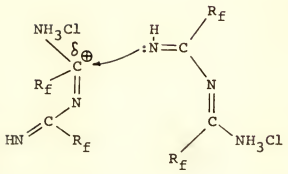
propyl)-1,3,5-triazine and 11 per cent of 2,4,6-tris(perfluoroethyl)-1,3,5-triazine.



XXV

As a matter of speculation it would appear that, contrary to prediction, the carbon atom of the amino hydrochloride group is more electrophilic than the carbon atom of the nitrile group. The major reaction product suggests preferential attack on the amino hydrochloride carbon atom as shown in XXVI. The presence of 2,4,6-tris(perfluoroethyl)-1,3,5-triazine may be accounted for by simple catalytic trimerization of the nitrile in the presence of hydrogen chloride.

XXVI

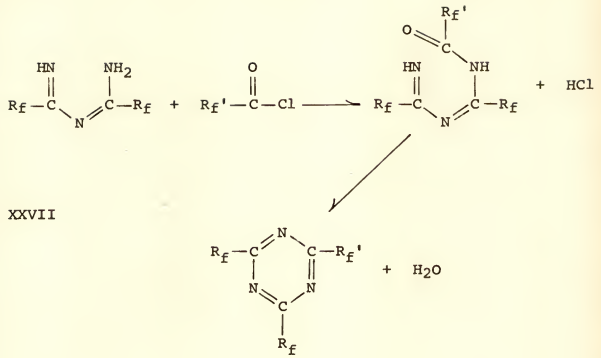


No exhaustive study was made of this system since it appeared that the reaction could not be used for the preparation of the desired sym-triazine, XXV(C).

Reaction of Perfluoropropionyl Chloride with N'(Perfluorobutyrimidoyl)perfluoro-butyramidine

In a further attempt to utilize the imidoyl-amidines for the preparation of a sym-triazine substituted with one R_f' and two R_f groups the reaction of an acid chloride with an imidoyl-amidine was considered. The reaction sequence is shown in XXVII.

The condensation product, hydrogen chloride, may in turn react to form the imidoyl-amidine hydrochloride. It was considered probable that carrying out this reaction in a sealed ampule, followed by heating, would result in dehydration of the acylated imidoyl-amidine and at the same



XXVII

time the imidoyl-amidine hydrochloride would condense to give a mixture of two triazines, 2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5-triazine and 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

In carrying out this reaction in a sealed glass ampule by reacting N'(perfluorobutyrimidoyl)perfluorobutyramidine with a sufficient excess of perfluoropropionyl chloride to act as a dehydrating agent, it was found that acylation and dehydration occurred at a relatively low temperature, 60-70°. Approximately 50 per cent of the reaction product, under these conditions, was a mixture of triazines,

96 per cent of which was the desired compound, 2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5 triazine. The remaining 4 per cent was 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

It is interesting to note that formation of the imidoyl-amidine hydrochloride should not interfere with the acylation reaction since the imidoyl-amidine hydrochloride will also undergo acylation.

Although no extensive study was made of this reaction it would appear to present an excellent method for the preparation of a linear polymer chain containing the sym-triazine ring connected by perfluoroalkyl groups. The value of this reaction, as a polymer-forming reaction, would depend on the extent of conversion to triazine possible. Although in the reaction of an acid chloride with the imidoyl-amidine conversion to triazine was on the order of 50 per cent, subsequent reactions of N'(perfluorobutyrimidoyl)perfluorobutyramidine with perfluoropropionic anhydride gave triazine yields in excess of 90 per cent. This anhydride reaction is not useful in polymer formation but does present an excellent method for the preparation of sym-triazines containing unlike substituents on the ring. In addition

the high yields obtained in this reaction are an encouraging sign for the success of the acid chloride reaction as a method for preparing polymers.

CHAPTER III

EXPERIMENTAL

Source of Materials

Perfluoroacetic, perfluoropropionic, perfluorobutyric and perfluorooctanoic acids were purchased from Columbia Organic Chemicals Company, Columbia, South Carolina. Perfluoroglutaronitrile was supplied by Hooker Chemical Company, 1940 Ward Street, Niagara Falls, New York. Deuterium oxide was purchased from Isomet Corporation, 431 Commercial Avenue, Palisades Park, New Jersey.

Perfluoroacetonitrile, perfluoropropionitrile, perfluorobutyronitrile and perfluorocaprylonitrile were prepared by dehydration of the perfluoroalkylamides as described by Swarts[18] and by Gilman and Jones.[19] Perfluoroalkylamidines, perfluoroglutarimidine and their N-methyl derivatives were prepared by the method of Reilly and Brown.[2]

Condensation of Perfluorobutyramidine

Deammonation of perfluorobutyramidine in pentachloroethane

A 500-ml. 3-neck flask was equipped with a reflux condenser, mechanical stirrer, thermometer, and a nitrogen inlet tube. The outlet of the condenser was connected by rubber tubing to a two-way stopcock. In addition a capillary tube was arranged for periodic removal of small samples (approximately 0.5 ml.) from the reaction mixture for examination of their infrared spectra.

The reaction vessel was heated to 110 $\pm$ 0.3° in a constant temperature oil bath and 300 ml. of a solution of perfluorobutyramidine in pentachloroethane containing 31.79 g. (149.9 millimoles) of solute was added. A slow sweep of dry nitrogen was run continuously through the apparatus and bubbled through known amounts of standard acid. It was possible to determine periodically the quantity of ammonia evolved without having to stop the gas flow by switching the gas flow through the two-way stopcock. Table 7 shows the results of this experiment and the point at which 0.5 ml. samples were removed for infrared analysis.

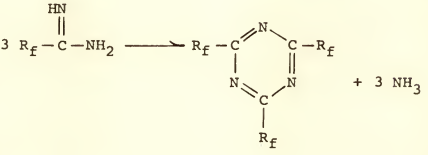
TABLE 7

DEAMMONATION OF PERFLUOROBUTYRAMIDINE
IN PENTACHLOROETHANE AT 110°

Elapsed Time Min.	Sample for Infrared Analysis	Millimoles of NH_3 Evolved	Calcd. Triazine Present, Grams
56	1	9.28	1.7
108	2	31.98	5.7
340	3	62.40	11.1
710	4	80.07	14.3
1,410	5	95.48	17.0
3,600	-	117.80	21.0

The first sample of the reaction solution which exhibited an infrared absorption maximum at 6.4 μ was that of sample #3. At this point in the reaction 41.6 per cent of the theoretical amount of ammonia had been evolved. This maximum corresponds to that of C=N stretching frequency in the conjugated cyclic system of the perfluoroalkyl-substituted sym-triazines.[2] Subsequent samples of the reaction solution showed increasing absorption at 6.40 μ, indicating a further increase in the triazine concentration on continuing the reaction.

The theoretical triazine concentration at any given period during the reaction may be calculated from the amount of ammonia evolved based on the following reaction sequence.

XXVIII 

This information is tabulated in the last column of Table 7 and indicates a triazine concentration of 2.5 per cent or 11.1 g. at the point of first appearance of absorption at 6.40 μ (sample 3). The room temperature solubility of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine in pentachloroethane was found to be only 0.9 per cent. Comparison of the intensity of the infrared absorption maximum at 6.4 μ of a prepared saturated solution of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine in pentachloroethane with that of samples taken from the reaction solution indicated saturation to have occurred approximately 1,410 minutes after the start of the reaction. It appeared from this that a product other than triazine was being formed. This was further substanti-

ated by finding that infrared maxima other than that due to the amidine, in the region of 2.7 to 3.2 μ (N-H stretching frequency), appeared early in the reaction and intensified as the reaction proceeded.

At termination of the reaction the reaction mixture was found to be clear and one phase.

Isolation of N'(perfluorobutyrimidoyl)perfluorobutyramidine as an intermediate in the deammonation of perfluorobutyramidine

Exhaustive attempts at isolating the suspected N'(perfluorobutyrimidoyl)perfluorobutyramidine from the reaction solutions used in the early deammonation studies were in general unsuccessful. By cooling the reaction mixture in a dry ice-acetone slurry and filtering the resulting precipitate it was possible to obtain a small amount of impure N'(perfluorobutyrimidoyl)perfluorobutyramidine.

In order to reduce the complicating factor of isolating the product from dilute solutions the condensation reaction was carried out by heating perfluorobutyramidine at its melting point. In addition to this simplification, isolation of this intermediate as a metal chelate was considered possible.

Perfluorobutyramidine, 2.17 g. (1.02×10^{-2} moles), was placed in a small Pyrex tube fitted with a gas inlet and outlet tube. The amidine was heated in an oil bath at 100° for 5.0 hours under a dry nitrogen sweep. After approximately one-third of the theoretical amount of ammonia was evolved the tube was cooled to room temperature and was found to contain a mixture of liquid and solids. The liquid, approximately 0.3 g., was removed by filtration and treated with a 5 per cent solution of copper(II) acetate. An immediate pink, hydrophobic precipitate resulted. After crystallization from carbon tetrachloride and drying on a porous clay plate, the chelate had a melting point of 148.5 to 149.5°. This product was subsequently identified as N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate by comparison with an authentic sample prepared at a later date (Table 2).

Preparation of N'(Perfluoroacylimidoyl)-perfluoroalkylamidines

N'(Perfluorobutyrimidoyl)perfluoro-butyramidine

Into an evacuated heavy-wall Pyrex glass ampule of approximately 50 ml. capacity, previously constricted for

sealing, were condensed perfluorobutyronitrile, 35.5 g. (6.95×10^{-2} moles), and anhydrous ammonia, 0.391 g. (2.30×10^{-2} moles), the ampule being cooled by liquid nitrogen.

In order to moderate the reaction exotherm the mixture was initially warmed to -78° and maintained at that temperature for 1 hour. Under these conditions the reaction tube contained a mixture of liquid and solid (perfluorobutyramidine). The ampule was then warmed to 0° and held at this temperature for 23 hours. At the end of this period the reaction tube was opened to the vacuum system. On warming the tube to room temperature, 4.72 g. (0.0242 moles) of unreacted perfluorobutyronitrile were recovered. Remaining in the reaction tube was a quantitative yield of water-white, liquid N'(perfluorobutyrimidoyl)perfluorobutyramidine, b.p. 44.3-44.7° (1.5 mm.). Other physical properties and analyses are given in Table 1.

N'(Perfluoropropionimidoyl)perfluoropropionamidine

Perfluoropropionitrile, 10.08 g. (6.95×10^{-2} moles), and anhydrous ammonia, 0.343 g. (2.02×10^{-2} moles), were allowed to react in a heavy-wall glass ampule, as described for the preparation of N'(perfluorobutyrimidoyl)perfluoro-

butyramidine. The ampule was opened after reaction and 0.131 g. (2.82×10^{-2} moles) of unreacted perfluoropropionitrile recovered. Remaining in the reaction tube was pure, water-white, liquid N'(perfluoropropionimidoyl)perfluoropropionamidine. The small amount of nitrile, 0.131 g. (9.0×10^{-4} moles), consumed in excess of the theoretical amount indicates essentially quantitative conversion to N'(perfluoropropionimidoyl)perfluoropropionamidine. The purity of this product was further substantiated by distillation, at reduced pressure, through a small, packed column with the entire product distilling at 35.9-36.1° (6.8 mm.). Other physical properties and analyses are shown in Table 1.

N'(Perfluoroacetimidoyl)perfluoroacetamidine

Into an evacuated heavy-wall Pyrex glass ampule of approximately 50 ml. capacity, cooled by liquid nitrogen, were condensed 6.79 g. (7.15×10^{-2} moles) of perfluoroacetonitrile and 0.394 g. (2.32×10^{-2} moles) of anhydrous ammonia. The reaction tube was warmed to -78° and held at this temperature for 30 minutes, then warmed to -24° and held at this temperature for one hour. Under these conditions the reaction mixture was converted to a white solid.

The reaction tube was then warmed to 0°, reopened to the vacuum system, and 2.09 g. (2.20×10^{-2} moles) of unreacted perfluoroacetonitrile recovered. Remaining in the reaction tube was 5.09 grams of a white, crystalline N'(perfluoroacetimidoyl)perfluoroacetamidine, m.p. 38-42°. The additional nitrile consumed, 0.295 g. (3.1×10^{-3} moles), over the theoretical amount was shown in earlier experiments to be converted to 2,4,6-tris(perfluoromethyl)-1,3,5-triazine. When this reaction was carried out using smaller quantities of reactants, with better thermal control, it was possible to obtain quantitative conversion. Some difficulty was encountered in storage and analysis of N'(perfluoroacetimidoyl)perfluoroacetamidine since it hydrolized rapidly on exposure to the atmosphere; the hydrolysis product is presumed to be analogous to that of N'(perfluorobutyrimidoyl)-perfluorobutyramidine which hydrolized to N(perfluorobutyryl)perfluorobutyramidine on exposure to atmospheric moisture.

N'(perfluoroacetimidoyl)perfluoroacetamidine decomposed slowly at room temperature, in the absence of moisture, to a liquid-solid mixture of undetermined composition. Other physical properties and analyses are shown in Table 1.

N'(Perfluoroacetimidoyl)perfluoro-
butyramidine

Perfluorobutyramidine, 25.91 g. (1.22×10^{-1} moles), was placed in a 250-ml. flask containing a Teflon-coated stirring bar. The flask was attached to a calibrated vacuum system and pumped free of air. Measured amounts of perfluoroacetonitrile were brought in contact with the solid perfluorobutyramidine at an average pressure of 400 mm. while the reaction mixture was maintained at 0°. After approximately 50 per cent of the theoretical amount of nitrile had reacted the reaction mixture was sufficiently fluid for stirring. Stirring was continued over a period of 8 hours. During this 8-hour period a pressure of perfluoroacetonitrile was maintained over the reaction mixture. At the end of this time 99 per cent (11.48 g., 1.21×10^{-1} moles) of the theoretical amount of nitrile had reacted. Continued exposure of the reaction mixture to perfluoroacetonitrile resulted in no further reaction. The liquid product was distilled through a packed column at reduced pressure to yield pure N'(perfluoroacetimidoyl)perfluorobutyramidine, b.p. 47.0-48.0° (7 mm.). On storage at room temperature in sealed tubes this product slowly decomposed to unidentified products. Other physical properties and analyses are shown in Table 1.

N'(Perfluoropropionimidoyl)perfluoro-butyramidine

Perfluorobutyramidine, 10.92 g. (5.15×10^{-2} moles), was placed in a heavy-wall Pyrex glass ampule of approximately 50-ml. capacity. The ampule was constricted for sealing and pumped free of air. Perfluoropropionitrile, 9.70 g. (6.69×10^{-2} moles), was condensed into the ampule using liquid air as coolant. The ampule was sealed, warmed to room temperature and held at this temperature for 48 hours. The ampule was reopened to the vacuum system and unreacted perfluoropropionitrile, 3.87 g. (2.67×10^{-2} moles), was recovered. Remaining in the reaction tube after removal of the unreacted nitrile was 16.7 g. of a clear liquid. Distillation at reduced pressure through a packed column gave a yield of 81 per cent of N'(perfluoropropionimidoyl)perfluorobutyramidine, b.p. 39.2-40.0° (3.8 mm.). Other physical properties and analyses are shown in Table 1.

On storage under vacuum over a period of ten months this product was converted largely into a mixture of perfluoroalkyl-substituted sym-triazines. The proportions of the various triazines found are shown in Table 6.

N'(Perfluorocaprylimidoyl)perfluorobutyramidine

Perfluorobutyramidine, 3.24 g. (1.04×10^{-2} moles), was dissolved in 25 ml. of methylene chloride and the solution was added to a 200-ml. flask equipped with a reflux condenser, a nitrogen sweep inlet tube and a dropping funnel. While stirring with a magnetic stirrer, perfluorocaprylonitrile, 6.62 g. (1.68×10^{-2} moles), b.p. 103-104°, dissolved in 60 ml. of methylene chloride, was added over a period of 20 minutes with the reaction mixture maintained at a temperature of 30°. After complete addition of the nitrile the reaction mixture was heated to reflux temperature and maintained at reflux for 3 hours. The methylene chloride solvent was removed at reduced pressure yielding 8.33 g. of a slightly viscous, cloudy liquid which presumably contained excess perfluorocaprylonitrile. N'(perfluorocaprylimidoyl)perfluorobutyramidine was isolated only as its copper(II) chelate. Other physical properties and analyses are shown in Table 2.

N(Perfluorobutyrimidoyl)-N-methylperfluorobutyramidine

Perfluorobutyronitrile, 13.22 g. (6.78×10^{-2} moles), and methylamine, 0.71 g. (2.26×10^{-2} moles), were sealed in

a heavy-wall glass ampule and allowed to react in a stepwise manner as described for the preparation of N'(perfluorobutyrimidoyl)perfluorobutyramidine. N-methyl-perfluorobutyramidine was formed initially at -78°; this product, when warmed to 0°, reacted in turn with the excess nitrile present. Unreacted perfluorobutyronitrile, 1.13 g. (5.8×10^{-3} moles) was recovered leaving a solid-liquid mixture in the reaction tube. The solids were separated by filtration and crystallized from hexane to give 2.55 g. (37 per cent) of white, crystalline N(perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine, m.p. 45.5-47.0°. Analysis, calculated for $C_9H_3F_{14}N_3$: C, 25.65; H, 1.19; N, 9.99. Found: C, 25.86; H, 1.33; N, 9.88.

Reactions of the N'(Perfluoroacylimidoyl)-perfluoroalkylamidines

Preparation of metal chelates, N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate

N'(perfluorobutyrimidoyl)perfluorobutyramidine, 5.43 g. (1.33×10^{-2} moles), was dissolved in 100 ml. of carbon tetrachloride and mixed vigorously with an excess of aqueous 5 per cent copper acetate solution. A pink-colored precipitate formed immediately, with the water

layer becoming decidedly acidic. The precipitate was removed by filtration and the carbon tetrachloride layer separated and evaporated to dryness under reduced pressure. The combined solid product was washed with water and dried at 110° to yield 5.75 g. (98 per cent) of N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate, m.p. 148.5-149.5°.

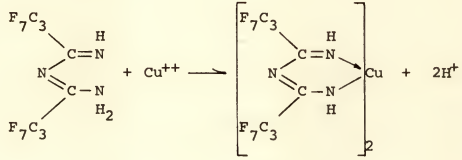
The additional chelates shown in Table 2 were prepared in essentially the same manner and in comparable yields.

Titration of N'(perfluoroacylimidoyl)perfluoroalkylamidines with copper(II) acetate

The method used for determination of the copper equivalent or molecular weight of some of the imidoyl-amidines by titration with standard copper(II) acetate solution is outlined in the following typical example.

N'(perfluorobutyrimidoyl)perfluorobutyramidine, 1.2926 g., was dissolved in 100 ml. of 60 volume per cent aqueous ethanol. This solution was titrated with a freshly prepared copper(II) acetate solution, 0.0500 molar with respect to cupric ion. The course of the titration was followed by determining pH at intervals during the titration.

For this specific example the end point of the titration was found at 30.9 ml., as shown in Figure 2. This end point indicates a copper equivalent for N'(perfluorobutyrimidoyl)-perfluorobutyramidine as 836 g. per gram atom of copper. Based on the following reaction then the molecular weight

XXIX 

of N'(perfluorobutyrimidoyl)perfluorobutyramidine is 836/2 or 418 as determined by titration while the calculated theoretical molecular weight is 407.

Thermal decomposition of N'(perfluorobutyrimidoyl)perfluorobutyramidine

N'(perfluorobutyrimidoyl)perfluorobutyramidine, 5.58 g. (1.37×10^{-2} moles), was placed in a 250-ml. reaction flask arranged with a nitrogen sweep to carry the volatile decomposition products through an ice-cooled trap, a liquid air-cooled trap, and finally through an oil-sealed bubbler. A second liquid air trap could be switched into

this line while the products from the first trap were being examined. The reaction flask was heated for the periods shown in Table 8, at the temperatures indicated. Periodic examination of the contents of the liquid air-cooled trap, during the course of reaction, revealed that this trap not only contained gaseous materials but also liquids and solids. Separation of a small amount of solid revealed it to be perfluorobutyramidine by comparison of its infrared spectra with an authentic sample of perfluorobutyramidine. The liquid product reacted with copper acetate solution to give a pink solid which was identified as N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate. Identification of the residue in the reaction flask by its infrared spectra showed that this material was identical with a known sample of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. Molecular weight of the gaseous products was determined by gas density method (Dumas).

A second decomposition run was made in a system similar to that described in the previous section with the exception that a phosphorous pentoxide tube was introduced between the ice-cooled trap and the liquid air-cooled trap. This tube was included in the system in order to remove

TABLE 8

THERMAL DECOMPOSITION OF N'(PERFLUOROBUTYR-IMIDOYL)PERFLUOROBUTYRAMIDINE

Time at Indicated Temp. Min.	Temp. Range	Product in Liquid Air Trap	Molecular Wt. of Gas	Weight G.
117	108-110	Liquid	--	0.02
		Gas	171	0.136
130	108-114	Liquid	--	0.01
		Gas	171*	0.03
115	114-122	Solid, liquid	--	0.02
		Gas	16.7	0.037
285	122-128	Solid, liquid	--	0.070
		Gas	17.3	0.059
1,380	128-130	Solid	--	0.28
		Gas	37	0.06
515	130	Solid, liquid	--	0.01
		Gas	67.3	0.01
825	140-153	Trace	--	--
		Total in liquid air trap		0.76
		Reaction flask residue		3.23
		Ice trap		1.26
		Total recovery		5.25
		Unrecovered material		0.33

*Assumed.

evolved ammonia and facilitate the separation of the perfluorobutyronitrile.

From 5.35 g. (1.31×10^{-2} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine, after a heating period similar to that shown in the previous run, was obtained 0.407 g. (2.08×10^{-3} moles) of perfluorobutyronitrile. By removal of ammonia from the system prior to condensation in the liquid air-cooled trap no solid or liquid was found in this trap. Identification of the nitrile from this reaction was confirmed by molecular weight (Dumas) and by comparative infrared spectra. The spectrum of the gaseous reaction product was identical with that of an authentic sample of perfluorobutyronitrile. The residue remaining in the reaction vessel was identified as 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

Reaction of perfluoropropionitrile with N'(perfluorobutyrimidoyl)perfluorobutyramidine

Into a heavy-wall Pyrex glass ampule of approximately 30-ml. capacity was placed 4.83 g. (1.18×10^{-2} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine. The ampule was cooled with liquid nitrogen, pumped free of air and 1.78 g. (1.23×10^{-2} moles) of perfluoropropioni-

trile added. The ampule was sealed, warmed to room temperature and placed in a vertical tube furnace at 130°. After 2 hours at temperature the liquid level increased, indicating that reaction had occurred. The ampule was removed from the furnace, cooled with liquid nitrogen, and opened to the vacuum system. Only a trace of condensable gases was found to be present. The resultant product was a slightly viscous, clear liquid which gave a strong positive test for triazine when treated with dioxane.* When a portion of the product was dissolved in carbon tetrachloride and the solution shaken with copper acetate solution, a slight pink coloration of the carbon tetrachloride layer appeared, indicating only a trace of imidoyl-amidine present.

The remainder of the product was heated to reflux, under a nitrogen sweep, for 24 hours until only a trace of ammonia was detected in the exit gases. A sample of the product was removed and analyzed chromatographically. It was found to contain a mixture of the four possible perfluoroalkyl-substituted sym-triazines. The product distribution is shown in Table 6.

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*See footnote, p. 89.

Additional reactions were run under various thermal conditions, time at temperature and molar ratios of reactants. These additional reaction products were examined chromatographically prior to refluxing the product as was done in the above example. The results of these additional runs are shown in Table 6.

Thermal decomposition of N'(perfluorobutyrimidoyl)-perfluorobutyramidine under vacuum

This experiment was carried out to determine whether the imidoyl-amidine will form triazine at 65°.

Into a 20-ml. capacity ampule previously constricted for sealing was added 3.33 g. (8.18×10^{-3} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine. The ampule was pumped free of air and sealed.

After heating the imidoyl-amidine at 63-67° for 181 hours the ampule was reopened to the vacuum system. A trace of condensable gases was removed from the ampule which was insufficient for molecular weight determination. The slightly viscous liquid remaining in the ampule was removed, examined chromatographically and found to contain approximately 50 per cent of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

Room temperature decomposition of N'(perfluoropropionimidoyl)perfluorobutyramidine

A sample of N'(perfluoropropionimidoyl)perfluorobutyramidine which had been prepared and distilled at 39.2-40.0° (3.8 mm.) and stored under vacuum at room temperature for 10 months was noted to have changed considerably in viscosity over this period of time. Examination of this product chromatographically revealed that it had decomposed during this time, forming a mixture of products, 73 per cent of which was a mixture of four perfluoroalkyl-substituted sym-triazines. The product distribution is shown in Table 6.

Preparation of N'(perfluorobutyrimidoyl)-perfluorobutyramidine hydrochloride

A solution of 3.2 g. (7.86×10^{-3} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine in dry ether was placed in a 100-ml. flask containing a magnetic stirring bar and fitted with a gas inlet tube which extended below the surface of the solution. A gas outlet tube was connected to a magnesium sulfate drying tube to prevent moisture from entering the system.

Hydrogen chloride was bubbled into the solution with stirring; after a short period of time a white precipitate formed. When complete saturation occurred, as evidenced by HCl in the exit gases, the addition of HCl was stopped.

The ether was evaporated under reduced pressure giving a dry, white, hygroscopic powder, N'(perfluorobutyrimidoyl)perfluorobutyramidine hydrochloride. When a small portion of this product was dissolved in water the water became acidic and a heavy liquid precipitated forming two layers. The lower, heavy layer was decanted and shaken with a solution of copper acetate resulting in the formation of a pink-colored precipitate which was identified, by its infrared spectra, as the copper chelate of N'(perfluorobutyrimidoyl)perfluorobutyramidine. On treating the upper water layer with copper acetate no chelate formation was observed.

Due to its hygroscopic nature, this compound was difficult to handle and attempts to determine its molecular weight, by titration, met with only fair success and were abandoned in favor of titration of the ligand with copper acetate as described on page 79.

Attempted reaction of N'(perfluorobutyrimidoyl)-perfluorobutyramidine hydrochloride with perfluoropropionitrile

Into a heavy-wall Pyrex ampule of approximately 20-ml. capacity was added 1.0 g. (2.46×10^{-3} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine. The ampule was cooled with liquid nitrogen, pumped free of air and hydrogen chloride, 0.158 g. (4.94×10^{-3} moles), and perfluoropropionitrile, 0.389 g. (2.68×10^{-3} moles), was added. The ampule was sealed and heated in a vertical tube furnace at 100° for 12 hours. At the end of this period only a trace of liquid was present, approximately 0.1 g. Vapor phase chromatographic analysis showed the product to be a mixture of two triazines, 89 per cent 2,4,6-tris(perfluoropropyl)-1,3,5-triazine and 11 per cent of 2,4,6-tris(perfluoroethyl)-1,3,5-triazine.

Reaction of perfluoropropionyl chloride with N'(perfluorobutyrimidoyl)perfluorobutyramidine

Into a heavy-wall ampule of approximately 100-ml. capacity was added 12.17 g. (2.99×10^{-2} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine. The ampule was cooled in liquid nitrogen, pumped free of air and perfluoro-

propionyl chloride, 13.58 g. (7.46×10^{-2} moles), was added. The ampule was sealed, warmed to room temperature then heated in a vertical tube oven at 60-70° for 15 hours. At the end of this time most of the solids in the ampule had disappeared and considerable liquid was present. After the heating period the ampule was reopened to the vacuum system and unreacted gases removed. The crude liquid product was removed from the tube and filtered giving 16.49 g. of a water-white filtrate and approximately 0.1 g. of white solid. The liquid product was poured into 1,4-dioxane forming an immediate white precipitate.* After removal of most of the excess dioxane by filtration the precipitate weighed 13.15 g. This dioxane adduct was placed in a separatory funnel and shaken vigorously with a 5 per cent hydrochloric acid solution, freeing the triazine which separated as a heavy lower layer weighing 8.54 g.

Vapor phase chromatographic analysis of the isolated product showed it to be a mixture of 96 per cent (8.2 g.) of

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*An observation made in this laboratory, by Mr. M. Cheng, that liquid perfluoroalkyl-substituted sym-triazines form a solid complex with dioxane has been used as a qualitative test for the presence of triazine. It would also appear from the above decomposition of the crude adduct that the proportion of dioxane to triazine approximates a 3 to 1 molar ratio.

2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5-triazine and 4 per cent (0.34 g.) of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. This represents a 51.2 per cent yield of the desired product based on the amount of N'(perfluorobutyrimidoyl)-perfluorobutyramidine reacted.

Crude products from a number of experiments were combined and distilled through an efficient, packed distillation column giving chromatographically pure 2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5-triazine, b.p. 151-152°; n^{25} 1.3101, d^{25} 1.6949. Analysis, calculated for $C_{11}F_{19}N_3$: C, 24.67; F, 67.47; N, 7.58. Found: C, 24.89; F, 67.20; N, 7.91.

Reaction of N'(perfluorobutyrimidoyl)perfluorobutyramidine hydrochloride with perfluoropropionyl chloride

Into a 100-ml. heavy-wall Pyrex glass ampule, previously constricted for sealing, was placed 8.43 g. (2.07×10^{-2} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine. The ampule was pumped free of air and hydrogen chloride, 0.907 g. (2.52×10^{-2} moles) was measured in the vacuum system then allowed to react with the imidoyl-amidine by opening the ampule to the vacuum system. A white solid formed immediately. After 2 hours contact time, at an

average pressure of 300 mm., the reaction was complete and excess hydrogen chloride was removed.

After formation of the N'(perfluorobutyrimidoyl)perfluorobutyramidine hydrochloride the ampule was cooled with liquid nitrogen and perfluoropropionyl chloride, 5.55 g. (3.05×10^{-2} moles) was added. The ampule was sealed, warmed to room temperature, then placed in a vertical tube oven at 150°. After 1/2 hour in the oven considerable liquid was noted in the bottom of the tube indicating that reaction had occurred. After heating for an additional 7 hours the liquid level remained unchanged from that first observed and the ampule was removed from the oven.

The ampule was cooled with liquid nitrogen, reopened to the vacuum system and 4.76×10^{-2} moles of gas, having an average molecular weight of 50.2 g., was recovered.

No attempt was made to isolate the products of this reaction; however, a small portion of the product was examined chromatographically and found to be composed of 92 per cent of 2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5-triazine and 8 per cent of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

Reaction of perfluoropropionic anhydride with N'(perfluorobutyrimidoyl)perfluorobutyramidine

To 5.0 g. (1.2×10^{-2} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine in a 50-ml. flask was slowly added 15 g. (4.8×10^{-2} moles) of perfluoropropionic anhydride. Immediately on addition of the anhydride a white solid formed with the evolution of a considerable amount of heat. On continued addition of the anhydride the white solid slowly dissolved resulting in a clear solution. The reaction mixture was transferred to a separatory funnel, washed with water and the lower layer decanted, yielding 5.96 g. (91 per cent) of a clear liquid product identified chromatographically as 2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5-triazine.

Reaction of ammonia with N'(perfluorobutyrimidoyl)perfluorobutyramidine

Into a 20-ml. glass ampule was placed 1.03 g. (2.53×10^{-3} moles) of N'(perfluorobutyrimidoyl)perfluorobutyramidine. The ampule was attached to the vacuum system, pumped free of air, cooled with liquid nitrogen and an excess of anhydrous ammonia added. The ammonia was allowed to expand into the vacuum system and maintained in contact with

the N'(perfluorobutyrimidoyl)perfluorobutyramidine for 5 hours. At the end of this time the excess ammonia was pumped off leaving a white crystalline residue. The infrared spectrum of this compound was found to be identical with that of perfluorobutyramidine.

Preparation of N(perfluorobutyryl)perfluorobutyramidine

Perfluorobutyric anhydride, 30.0 g. (7.31×10^{-2} moles), was placed in a 100-ml. flask containing a Teflon-covered magnetic stirring bar. Perfluorobutyramidine, 4.0 g. (1.88×10^{-2} moles), was added slowly with stirring while the temperature was maintained at 30°. After addition was completed the reaction mixture was poured into water, extracted with ether and the ether extract repeatedly washed with water. Evaporation of the ether solution at reduced pressure gave 6.1 g. of N(perfluorobutyryl)perfluorobutyramidine which was found to be soluble in dilute aqueous alkali and could be precipitated from the basic solution on acidification. Recrystallization from tetrahydrofuran gave white, crystalline N(perfluorobutyryl)perfluorobutyramidine, m.p. 224° (dec.). Analysis calculated for

$C_8H_3F_{14}N_2O$: C, 23.45; H, 0.49; N, 6.85. Found: C, 23.79; H, 0.43; N, 6.68.

When N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate was dissolved in concentrated sulfuric acid and immediately diluted with water, a white crystalline product resulted which was found to have an identical melting point and infrared spectrum with N(perfluorobutyryl)perfluorobutyramidine. An identical product results on exposure of N'(perfluorobutyrimidoyl)perfluorobutyramidine to atmospheric moisture over a long period of time.

Reaction of Ammonia with a Mixture of Perfluoroalkyl-Substituted sym-Triazines

Into a heavy-wall Pyrex glass ampule of approximately 20-ml. capacity was added 0.74 g. (1.70×10^{-3} moles) of 2,4,6-tris(perfluoroethyl)-1,3,5-triazine and 2.0 g. (3.42×10^{-3} moles) of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. The ampule was pumped free of air, cooled with liquid nitrogen and 0.0296 g. (1.74×10^{-3} moles) of ammonia was added. On sealing the ampule and warming to room temperature, the originally liquid triazine mixture was converted to a white solid. This solid was presumably the triazine-

ammonia adduct which has been encountered numerous times but has not been characterized.

The ampule was placed in an oil bath at 100° at which temperature the solid melted and separated into two liquid layers. The bottom layer was clear yellow-brown and the upper layer clear white. After 21 hours at 100° the ampule was cooled with liquid nitrogen and reopened to the vacuum system and condensable gases removed. The resultant product was a viscous, yellow-brown liquid which was analyzed chromatographically and found to be a mixture of all four possible perfluoroalkyl-substituted sym-triazines. The proportions of the various triazines present are shown in Table 6.

Vapor Phase Chromatographic Separation and Identification of Perfluoroalkyl-Substituted sym-Triazines

It was found that mixtures of the various perfluoroalkyl-substituted sym-triazines encountered in this study could be separated chromatographically. An Aerograph Model A-100-C vapor phase chromatograph was standardized for this purpose. The sample being examined was injected into a heated injection chamber maintained at 125°. Helium was used as the carrier gas with a flow rate of 0.23 ml./sec.

The chromatographic column was 1 meter of 1/4-inch copper tubing packed with Celite with Kel-F #90 grease as the stationary phase. The column was heated to 86° during operation. Under these conditions the apparatus was standardized with pure 2,4,6-tris(perfluoropropyl)-1,3,5-triazine and 2,4,6-tris(perfluoroethyl)-1,3,5-triazine having 28.1 and 8.9 minutes appearance times respectively. The sym-triazines substituted with unlike perfluoroalkyl groups were identified by interpolation of flow times they exhibited. The greater appearance time was assigned to that of the higher molecular weight triazine. Typical appearance times are shown below.

Triazine	Appearance Time
$(C_2F_5CN)_3$	8.9 min.
$(C_2F_5CN)_2(C_3F_7CN)$	12.4 min.
$(C_3F_7CN)_2(C_2F_5CN)$	17.6 min.
$(C_3F_7CN)_3$	28.1 min.

Preparation of Ammonia-d_3

Deutero ammonia, ND_3, was prepared by a slightly modified method of Taylor and Jungers.[21]

A total of 150 g. of magnesium turnings was heated, in separate 50-g. portions, by a Meker burner in a small

crucible covered with sheet asbestos in which a 1/16-inch hole had been cut. After heating by direct flame for approximately 15 minutes, the crucible was removed from the flame and the magnesium allowed to react with the nitrogen and oxygen of the atmosphere. This procedure produced principally magnesium nitride, Mg_2N_3. The magnesium nitride was heated at 100° for 8 hours under vacuum to remove NH_3 formed by reaction with atmospheric moisture, then stored under dry nitrogen.

The flask containing the magnesium nitride was equipped with a nitrogen sweep and D_2O was added slowly. The ND_3 formed was condensed from the nitrogen sweep by a trap immersed in a dry ice-acetone slurry.

The addition of 78 g. of D_2O over a period of 4 hours produced 9.2 g. of dry ND_3. Infrared spectra of this product (75 mm. pressure in a 50-mm. cell) showed none of the strong absorption bands of the NH_3 spectra.

Preparation of Compounds Containing the N-D Bond for Infrared Analysis

N'(Perfluorobutyrimidoyl)perfluorobutyramidine-d_3

Perfluorobutyronitrile, 5.74 g. (2.94×10^{-2} moles), and ammonia-d_3, 0.062 g. (3.1×10^{-3} moles), were condensed

into an evacuated 10-ml. glass ampule; the ampule was sealed and held at room temperature for 46 hours. The ampule was then opened to the vacuum system and 4.52 g. (2.32×10^{-2} moles) of unreacted perfluorobutyronitrile recovered, leaving a quantitative yield of N'(perfluorobutyrimidoyl)perfluorobutyramidine-d_3.

Perfluorobutyramidine-d_3

Perfluorobutyronitrile, 1.03 g. (5.3×10^{-3} moles), and ammonia-d_3, 0.114 g. (5.7×10^{-3} moles), were sealed in a previously evacuated glass ampule and held at room temperature for 4 hours. The ampule was then opened to the vacuum system and the excess ammonia-d_3 removed to leave white, crystalline perfluorobutyramidine-d_3, m.p. (after washing with hexane) 54-56°.

Perfluoroglutarimidine-d_3

This preparation was similar to that described above for the preparation of perfluorobutyramidine-d_3.

Perfluorobutyramide-d_2

Approximately 1.0 ml. of methyl perfluorobutyrate was added to an ampule of 10-ml. capacity. The ampule was

attached to the vacuum system, cooled in liquid nitrogen and pumped free of air. An excess of ammonia-d_3 was condensed in the ampule and the mixture allowed to warm slowly. Repeated evaporation and condensation of the ammonia-d_3 gave a white crystalline solid, perfluorobutyramide-d_2. The ampule was pumped free of excess ammonia-d_3 and methyl alcohol and sealed.

N'(Perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate-d_2

N'(perfluorobutyrimidoyl)perfluorobutyramidine was prepared as described above from 4.0×10^{-4} moles of ammonia-d_3 and excess perfluorobutyronitrile in a 10-ml. ampule. A saturated solution (2 ml.) of $Cu(OAc)_2 \cdot H_2O$ in D_2O was introduced into the ampule by a hypodermic needle through the rubber tubing connecting the reaction tube to the vacuum system. The maroon-colored solid chelate formed immediately and the excess D_2O was removed under vacuum.

N(Perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine-d_2

Approximately 1 gram of N(perfluorobutyrimidoyl)-N-methyl-perfluorobutyramidine was placed in a 10-ml. glass ampule with 3 ml. of D_2O. The suspended imidoyl-amidine

was heated to 60° for 2 minutes followed by removal of the excess D_2O under vacuum.

Determination of the Approximate Rate of Deuterium Exchange

The deuterated compounds were exposed to the atmosphere at 45 per cent relative humidity and 28° for the times shown in Table 5. The approximate measure of exchange was determined by the appearance of or increase in the absorption maxima corresponding with the N-H stretching frequency.

Attempted Gas Phase Reaction of Perfluoroalkylnitriles with Ammonia

Perfluorobutyronitrile

At room temperature and at atmospheric pressure, perfluorobutyronitrile, 1.63×10^{-4} moles per minute, and anhydrous ammonia, 9.3×10^{-4} moles per minute, were continuously mixed by passing the gases initially to a "T" tube, through a 2-liter mixing flask and finally to a trap cooled by liquid air. This procedure was carried out for 50 minutes with no observable gas phase reaction occurring. After termination of flow the gaseous mixture was sealed

from the atmosphere in the 2-liter reaction flask and left over night. After this time (approximately 16 hours) some perfluorobutyramidine had formed. The mixture which condensed in the liquid air trap, when warmed, also formed the perfluorobutyramidine.

Perfluoroacetonitrile

A gas phase reaction, similar to the previous run, was attempted using perfluoroacetonitrile in the same apparatus. The gases were mixed at the rate of 1.08×10^{-4} moles per minute of perfluoroacetonitrile and 5.0×10^{-4} moles per minute of anhydrous ammonia. After 35 minutes flow no apparent reaction was noted in the reaction flask. It was found, however, that some reaction was occurring at the "T" junction where initial mixing occurred. When the liquid air-cooled trap was warmed, perfluoroacetamidine was formed. When the gaseous mixture was retained in the mixing flask over night, liquid perfluoroacetamidine was formed.

On further treatment of the perfluoroacetamidine formed in the mixing flask with additional perfluoroacetonitrile under static conditions (adding perfluoroacetonitrile periodically to the system) a crystalline product formed

which was identified by its infrared spectrum as N'(perfluoroacetimidoyl)perfluoroacetamidine.

Effect of Ammonium Chloride on the Perfluoroalkyl-Substituted sym-Triazines at High Temperature

Into an ampule of approximately 20-ml. capacity was placed 2,4,6-tris(perfluoropropyl)-1,3,5-triazine, 1.0 g. (1.71×10^{-3} moles), 2,4,6-tris(perfluoroethyl)-1,3,5-triazine, 1.0 g. (2.3×10^{-3} moles) and 0.1 g. of ammonium chloride. The ampule was pumped free of air and sealed. The mixture was then heated to 150° for 3 hours. On reopening to the vacuum system no condensable gases were found. After removal of the ammonium chloride by filtration vapor phase chromatographic analysis revealed that the original triazines had remained unchanged.

CHAPTER IV

SUMMARY

The reaction studied was the condensation of the perfluoroalkyl amidines. Elucidation of the mechanism of this reaction was attempted in a study of the kinetics of the deammonation of perfluorobutyramidine. The results of these experiments indicated the presence of a stable "dimeric" intermediate which was subsequently isolated from the condensation reaction mixture as its copper(II) chelate. The chelate was identified as N'(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate. Based on the identification of this intermediate a mechanism was proposed for this initial part of the condensation reaction.

Further research revealed that the reaction intermediate, N'(perfluorobutyrimidoyl)perfluorobutyramidine, could be prepared, exclusive of the condensation reaction, by the addition of perfluorobutyramidine to perfluorobutyronitrile. A series of these compounds, containing different perfluoroalkyl groups, were prepared and characterized. Characterization of these compounds and some of their metal

chelates showed that the N'(perfluoroacylimidoyl)perfluoroalkylamidines exhibit absorption in the ultraviolet region of the spectrum, at 262 mμ. Finding that the imino group, as an isolated chromophore, does not exhibit absorption above 220 mμ suggested that the absorption shown by the N'(perfluoroacylimidoyl)perfluoroalkylamidines was due to conjugation of the imino group. A conjugated "enolic" structure was proposed for these compounds. Substantiation for this proposed structure was derived from the absorption spectra of a series of fluorocarbon derivatives which contained the imino group. Comparison of the ultraviolet spectra of these compounds with that of N'(perfluorobutyrimidoyl)perfluorobutyramidine suggested a further extension of the conjugated system through intra-molecular hydrogen bonding.

Replacement of the "chelated" hydrogen by a metal caused a bathochromic shift in the ultraviolet region of the spectrum indicating metal-donor interaction characteristic of this type of covalently bonded complex.

With the aid of deuterated compounds infrared absorption assignments were made between 2.5-6.6 μ for N'(perfluorobutyrimidoyl)perfluorobutyramidine, its copper chelate and for a number of related fluorocarbon derivatives.

A secondary objective of this study was accomplished in the preparation of 2,4-bis(perfluoropropyl)-6-perfluoroethyl-1,3,5-triazine. This compound was prepared by dehydration of the reaction product of perfluoropropionic anhydride or perfluoropropionyl chloride with N'(perfluorobutyrimidoyl)-perfluorobutyramidine. Reaction of the acid chloride presents a method for the preparation of a linear polymer chain containing the sym-triazine ring connected by perfluoroalkyl groups.

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BIOGRAPHICAL SKETCH

Paul D. Schuman was born May 17, 1921, at Hillside, New Jersey. In June of 1938 he was graduated from Hillside High School. Following high school he was employed by Celanese Corporation as a laboratory technician until early 1941, at which time he entered the United States Navy as an Apprentice Seaman. During his military service he was stationed at a number of naval shore stations in the U. S. and abroad. He also served aboard the U.S.S. Shangri-la and was discharged from the Navy late in 1945.

Following his naval service he attended Seton Hall University while working as a laboratory technician at Celanese Corporation Research Laboratories. He received his Bachelor of Science degree in chemistry in June, 1953. From 1953 until 1958 he worked as a chemist for Resistoflex Corporation, Roseland, New Jersey. During this period he attended the Polytechnic Institute of Brooklyn night graduate school. In 1958 he enrolled in the Graduate School of the University of Florida. He worked as a graduate research assistant in the Department of Chemical Engineering. From

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Paul D. Schuman is married to the former Ruthann Corlett and is the father of three children. He is a member of the American Chemical Society and Gamma Sigma Epsilon.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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